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31/02, B29B 7/88, C08J 3/22da Vinci, 44, I-20099 Sesto San Giovanni (IT). **PUPPI**, Cristiano [IT/IT]; Via Bellini, 24, I-22028 Guanzate (IT). **DUCOLI**, Giuseppe [IT/IT]; Via Ponchiari, 10, I-21053 Castellanza (IT). **ALBIZZATI**, Enrico [IT/IT]; Via Trieste, 2, I-28040 Lesa (IT).

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(74) Agents: **GIANNESI**, Pier, Giovanni et al.; Pirelli S.p.A., Viale Sarca, 222, I-20126 Milano (IT).

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60/309,166 2 August 2001 (02.08.2001) US(71) Applicant (for all designated States except US): **PIRELLI PNEUMATICI S.P.A.** [IT/IT]; Viale Sarca, 222, I-20126 Milano (IT).

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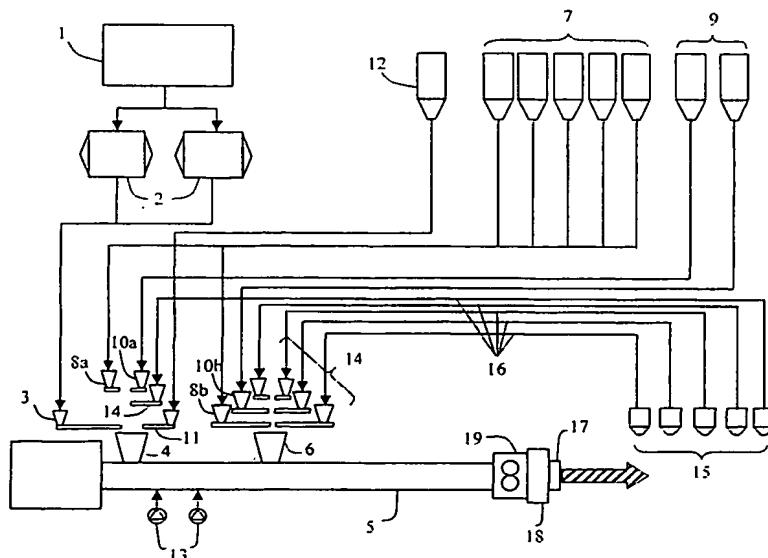
(72) Inventors; and

(75) Inventors/Applicants (for US only): **CARETTA**, Renato [IT/IT]; Viale dei Tigli, 16, I-21013 Gallarate (IT). **GALIMBERTI**, Maurizio [IT/IT]; Via Pannonia, 6, I-20133 Milano (IT). **AMURRI**, Cesare [IT/IT]; Via Leonardo

(54) Title: PROCESS AND APPARATUS FOR CONTINUOUSLY PRODUCING AN ELASTOMERIC COMPOSITION



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(57) Abstract: Process and apparatus for the continuous production of elastomeric compositions by means of at least one extruder, wherein the minor ingredients are used in the form of subdivided products, said products including at least one of the minor ingredients dispersed in a thermoplastic binding agent. Such products are conveyed to a dosing device by means of a pneumatic conveying line, and thus can be accurately metered and continuously fed into the extruder. The thermoplastic binding agent guarantees to the subdivided product free-flowing properties and high dimensional regularity and stability, even upon intense compression and/or friction stresses, such as those occurring in a pneumatic conveying line.



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PROCESS AND APPARATUS FOR CONTINUOUSLY PRODUCING AN ELASTOMERIC COMPOSITION.

The present invention relates to a process and 5 apparatus for continuously producing an elastomeric composition. More particularly, the present invention relates to a process and apparatus for continuously producing an elastomeric composition by means of at least one extruder, the resulting elastomeric composition being 10 primarily, but not exclusively, intended for use in the production of tyres.

Conventionally, the production of elastomeric compositions (in the following also indicated as "rubber mixtures") is performed batchwise by means of internal 15 mixers, usually Banbury mixers having two counter-rotating rotors which exert an intensive mixing action to masticate the rubber ingredients and to incorporate and thoroughly disperse therein the other ingredients, including fillers, lubricating aids, curatives and auxiliary substances.

20 The compounding process using internal mixers shows many drawbacks, particularly a poor heat dissipation and thus a scarce temperature control, mainly due to an unfavourable ratio between material volume and mixer surface area. To improve dispersion in the rubber base, 25 the various ingredients, and particularly the fillers, are incorporated into the rubber base in batches distributed in a plurality of mixing operations separated by cooling and stocking steps. Temperature sensitive ingredients, such as cross-linking agents and accelerators, are added 30 only during the final mixing step after cooling the rubber mixture below a predetermined temperature (usually below 110°C) to avoid scorching.

Therefore, the compounding process in internal mixers, although still remaining the most widely used 35 mixing process in the rubber industry, is time and energy consuming and does not guarantee an effective control on the characteristics of the resulting elastomeric

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compositions, particularly as regards dispersion homogeneity of fillers into the rubber base. Variation in the added amounts of individual ingredients, timing of addition and discharge from the mixers, initial 5 temperature of the raw materials, and fluctuations of shear forces inside the material during mixing, all contribute to batch-to-batch variation.

To overcome the limitations of the discontinuous processes, many attempts have been performed by the rubber 10 industry to set up continuous compounding processes, based on extrusion techniques analogous to those commonly employed in the processing of thermoplastic polymer materials. Continuous mixing processes carried out by means of an extruder should improve uniformity in the 15 rubber mixture characteristics, better thermal management resulting from improved surface-to-mass ratios, and possible development of highly automated operations. For an overview on this subject see the article "A tale of continuous development" by H. Ellwood, published in 20 *European Rubber Journal*, March 1987, pages 26-28.

US Patent No. 4,897,236 discloses a process and an apparatus for continuously producing a rubber mixture, wherein the ingredients of the mixture are fed, masticated and homogenized in a twin-screw extruder. The resulting 25 mixture is divided into a first and a second portion. The first portion is discharged, while the second portion is recycled for further homogenization and for mixing with fresh batches of the ingredients being fed into the extruder. The recycled portion is circulated to and 30 returned from a cooled, annular chamber exterior to the extruder chamber, said annular chamber having outflow and inflow passages communicating with the interior of the extruder. That partial recycling of the rubber mixture should compensate for fluctuations in the metering of the 35 ingredients and for local inhomogeneities which may occur. Moreover, the intensive cooling of the recycled portion in the annular chamber should correct a rising processing

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temperature, and should improve the dispersing action because of increased shearing stresses consequent to the temperature decrease.

US Patent No. 5,302,635 discloses a method and 5 apparatus for continuously producing a rubber composition. In a first step, crude rubber is continuously fed into a twin-screw extruder, added with non-reactive additives (oils and fillers) and the resulting mixture is plasticated and homogenized by the extruder screws. During 10 that first step, the mixture is kept at a temperature of from 100°C to 160°C. Then, in a second step, the resulting mixture is cooled to a temperature of from 100°C to 120°C and reactive additives (particularly sulfur and vulcanization accelerators) are fed and incorporated into 15 the rubber mixture. The homogenized end rubber composition then leaves the extruder via the extruder outlet opening.

The process can be carried out according to different extruder configurations. For instance, the two mixing steps can be performed in a single twin-screw extruder 20 having two distinct mixing zones operating at two different temperatures. Alternatively, the first step may be carried out in a first twin-screw extruder operating at 100°C-160°C; the resulting base composition is then fed directly to a second twin-screw extruder operating at 25 100°C-120°C. According to another embodiment, the process may be performed in a single extruder having two screw pairs driven at mutually opposite ends of the extruder housing, the two screw pairs operating at different temperatures.

30 US Patent No. 5,158,725 discloses a method for continuously producing elastomer compositions which comprises: feeding an elastomer into a twin-screw extruder; feeding at least one filler, oil and/or other elastomers into the extruder; mixing the ingredients to 35 provide a homogeneous mixture which is maintained at a Mooney viscosity ML(1+4) at 100°C between 20 and 250 during mixing; discharging the resulting mixture from the

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extruder. Precise volumetric or loss-in-weight feeders are used to meter the elastomer and other ingredients into the extruder. After leaving the extruder, the compounded rubber may be extruded through a die, calendered into 5 sheets, strips or strands, or may be pelletized. The continuous method is less expensive than the multi-step batchwise processes currently used in the art and requires less manpower and less material handling. Moreover, improved dispersion and homogeneity of the resulting 10 elastomeric compositions would result.

US Patent No. 5,262,111 discloses a process for the continuous production of a rubber composition in a twin-screw extruder. Rubber is fed into the extruder together with a processing aid and masticated up to a temperature 15 of 120°C to 180°C. Subsequently, a first part of carbon black, representing preferably 40-80% of the whole quantity of carbon black, is fed into the heated extrudate. Afterwards, plasticizing oil is added to the extrudate before the second remaining carbon black part is 20 fed and incorporated into the extrudate at a temperature of from 120°C to 180°C. The whole composition is then cooled to a temperature of from 100°C to 120°C, a crosslinking agent is added, and the composition is homogenized and extruded. The process would improve the 25 dispersion of carbon black in the extrudate while reducing the specific energy requirement.

US Patent No. 5,626,420 discloses a continuous mixing process and apparatus, wherein base elastomer(s) and other components are continuously dosed and introduced into a 30 mixing chamber formed of a stator and a rotor rotating therein, preferably a single screw extruder. The introduced components advance within the mixing chamber along zones of propulsion and mixing. To improve dispersion and homogenizing of the rubber components, the 35 filling rate of the mixing chamber in at least certain mixing zones is lower than 1. To properly introduce the components, and particularly the rubber base, into the

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mixing chamber, force feeding means are used, such as volumetric pumps (e.g. gear pumps). To obtain precise dosage of the different components, it may be desirable to add the components in a mixing zone where the filling rate 5 is equal to 1, located between two mixing zones having a filling rate lower than 1.

US Patent No. 5,374,387 describes a process for continuously producing elastomeric compositions using a twin-screw extruder, which comprises the following 10 sequential steps. In a first mixing zone of the extruder an elastomeric material is added, sheared and heated to a first operating temperature (typically from 130°C to 220°C) while reducing viscosity. Then the elastomeric material is passed in a second mixing zone where it is 15 added with at least a first portion of a reinforcing filler and processing aid, while simultaneously cooling the rubber mixture to a second operating temperature (typically from 110°C to 160°C). The resulting mixture is then passed to an optional third mixing zone, where small 20 constituent chemicals, such as adhesion promoters, anti-ozonants, color additives, fire retardants and the like, are introduced into the rubber mixture. Preferably, in said third mixing zone a second portion of the reinforcing filler and processing aid is added so as to reach a third 25 operating temperature (typically from 85°C to 130°C). Then, in a fourth mixing zone the rubber mixture is supplemented with the vulcanization agent at a fourth operating temperature (typically from 115°C to 150°C). The mixture flow is then directed through a delivery zone 30 (fifth zone) wherein the mixture flow is extruded into the desired form through some sort of die slot or the like. The various components of the rubber composition are continuously and individually metered to the extruder, preferably in the form of particulated materials and/or 35 liquids by means of weight loss feeders.

US Patent No. 5,711,904 discloses a method for continuous mixing of elastomeric compositions reinforced

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with silica. A twin-screw extruder is fed with the elastomeric material, then with silica and other compounding ingredients, including a silica coupler. Temperature and pressure along the extruder are controlled 5 to enable the silica coupler to react with the silica and the elastomeric material. Then curatives and accelerators are added, while maintaining the mixture at a Mooney viscosity ML(1+4) at 100°C between 20 and 250. The mixing is continued for a time sufficient to thoroughly mix the 10 curatives and accelerators. The resulting elastomeric composition is then forced through a suitable die mounted at the extruder exit. The overall process may be performed using a single extruder or a sequence of extruders. Preferably, residence time is increased in a first twin- 15 screw extruder and then the composition is cooled, ground and dumped into a second twin-screw extruder where the rubber mix is completed with curatives and other ingredients. The different extruders may be separate independent entities or may be coupled to each other to 20 form one continuous process. The extruders may be closely coupled in a cross-head extruder mounting, or may be more loosely connected, for instance via festoons or belts that convey the material from one unit to the other.

In the Applicant's view, one of the most critical 25 aspects in the production of an elastomeric composition by a continuous process is the addition to the rubber base of the so called "minor ingredients", which are those components different from rubbers, reinforcing fillers and plasticizing agents (e.g. vulcanizing agents, 30 vulcanization accelerators and retardants, protective agents, hardening resins, etc.), which are added to modify and/or to improve the characteristics of the elastomeric compositions. The minor ingredients are very numerous (usually at least 5-15 in a single rubber mixture) and 35 used in little amounts (generally not greater than 5% by weight with respect to the total weight of the rubber mixture). Types and amounts of the minor ingredients to be

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added vary according to the elastomeric composition to be produced.

Usually, in the discontinuous compounding processes the minor ingredients are managed off-line. They are 5 weighed as raw materials, charged into bags of a low melting material, sealed and automatically labelled with barcodes and alphanumeric data. Then, the labelled bags are manually introduced in the mixer hopper according to predetermined procedures which depend on the recipe of the 10 rubber mixture to be produced. A tyre manufacturer typically has to manage about 30-40 different minor ingredients.

The above off-line managing of the minor ingredients is totally unfeasible in a continuous compounding process, 15 where all the ingredients must be continuously and automatically dosed and fed into the extruder. The dosage shall be very accurate and the feeding shall proceed smoothly, since dramatic variations in the properties of the final rubber mixture may occur because of even little 20 fluctuations in the added amounts of the minor ingredients.

Furthermore, addition of the minor ingredients as raw, substantially pure products shows many shortcomings. Firstly, the raw products are usually in the form of 25 powders or of liquids, which are hardly dispersible in the rubber base and therefore require long mixing times. Additionally, an accurate continuous metering of little amounts of a concentrated product is difficult on an 30 industrial scale, particularly when the product is poorly flowable, for instance in the case of low melting compounds or materials which show electrostatic charge accumulation. Finally, the raw products may give off 35 vapours and/or powders which can cause unpleasant odours and safety problems, particularly in the case of noxious or toxic substances.

The Applicant has now found that a process for the continuous production of elastomeric compositions may be

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carried out in at least one extruder by using the minor ingredients in the form of subdivided products, said products including at least one of the minor ingredients dispersed in a thermoplastic binding agent. Such products  
5 are conveyed to a dosing device by means of a pneumatic conveying line, and thus can be accurately metered and continuously fed into the extruder. The thermoplastic binding agent guarantees to the subdivided product free-flowing properties and high dimensional regularity and  
10 stability, even upon intense compression and/or friction stresses, such as those occurring in a pneumatic conveying line. Therefore, the subdivided product is suitable for a pneumatic transportation and for an accurate dosage, substantially without formation of fine powders and  
15 undesired changes in shape and/or dimensions of the granules. Moreover, the thermoplastic binding agent readily melts when introduced into the extruder, thus acting as a processing aid, and remarkably improves dispersion of the minor ingredient into the rubber base,  
20 without causing any significant changes in the properties of the final elastomeric composition.

Therefore, in a first aspect the present invention relates to a process for continuously producing an elastomeric composition, comprising the steps of:

25 - providing at least one extruder comprising a housing, at least one screw rotatably mounted in said housing, said housing including at least one feed opening and a discharge opening;

- metering and feeding into said at least one extruder  
30 at least one elastomer and at least one filler;

- metering and feeding into said at least one extruder minor ingredients different from elastomers and fillers;

- mixing and dispersing said at least one filler and  
35 minor ingredients into said at least one elastomer by means of said at least one extruder;

- extruding the resulting elastomeric composition

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through said discharge opening;  
wherein at least one of said minor ingredients is  
conveyed, before metering and feeding into the extruder,  
by means of a pneumatic conveying line in the form of a  
5 subdivided product, said product including said at least  
one minor ingredient dispersed in at least one  
thermoplastic binding agent.

According to a preferred aspect, at least one  
plasticizing agent is further metered and fed into the  
10 extruder.

According to a preferred aspect, the subdivided  
product is metered and fed by means of a gravimetric  
feeder.

According to another preferred aspect, the subdivided  
15 product contains from 40% to 98% by weight, more  
preferably from 50% to 95% by weight, even more preferably  
from 70% to 85% by weight, of said at least one minor  
ingredient, with respect to the total weight of said  
product.

20 According to another preferred aspect, the subdivided  
product has a Shore A hardness not lower than 45 and a  
Shore D hardness not greater than 65. More preferably, the  
subdivided product has a Shore D hardness of from 20 to  
60. Shore A and Shore D hardnesses are measured according  
25 to ASTM Standard D2240-00.

According to the present invention, the subdivided  
product may be in any subdivided free-flowing form  
suitable for a pneumatic conveying, e.g. in the form of  
30 granules, pellets, beads, pearls and the like, having  
average dimensions generally of from 0.5 mm to 5 mm,  
preferably from 1 mm to 3 mm.

According to a further aspect, the present invention  
relates to an apparatus for continuously producing an  
elastomeric composition, comprising:

35 - at least one extruder comprising a housing, at least  
one screw rotatably mounted in said housing, said  
housing including at least one feed opening and a

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discharge opening;

- at least one first metering device to meter and feed into said at least one extruder at least one elastomer and at least one filler through said at least one feed opening;
- at least one second metering device to meter and feed into said at least one extruder minor ingredients different from elastomers and fillers, at least one of said minor ingredients being in the form of a subdivided product including said at least one minor ingredient dispersed in at least one thermoplastic binding agent;
- at least one pneumatic conveying line to convey said at least one minor ingredient in the form of a subdivided product from a storage bin to said at least one second metering device.

Minor ingredients that can be metered and fed in the form of a subdivided product according to the present invention may be selected, for instance, from:

- 20 (a1) crosslinking agents, such as:  
sulfur (usually in a soluble crystalline form or in a insoluble polymeric form, optionally dispersed in an oily phase); sulfur donors (e.g. alkylthiuram disulfides); organic peroxides;
- 25 (a2) crosslinking accelerators, such as:  
thiazoles, sulfenamides, guanidines, thiurams, dithiocarbamates, amines, xanthogenates;
- (a3) synthetic resins, such as alpha-methylstyrene resins, cumarone resins;
- 30 (a4) crosslinking activators, such as zinc compounds (e.g. ZnO, ZnCO<sub>3</sub>, fatty acid zinc salts);
- (a5) crosslinking retardants, such as carboxylic acids, phthalimide derivatives, diphenylamine derivatives;
- (a6) adhesion promoters, such as hexamethylentetramine (HMT), resocinol;
- 35 (a7) protective agents, such as aromatic diamines (e.g. N-(1,3-dimethylbutyl)-N'-p-phenylenediamine (6PPD)),

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dihydrochinoline derivatives, imidazole derivatives;

(a8) coupling agents, such as coupling agents for silica, particularly sulfur-containing hydrolyzable silanes (e.g. 3,3'-bis(triethoxy-silylpropyl)tetrasulfide 5 (TESPT));

(a9) condensation catalysts, such as metal carboxylates (e.g. dibutyltindilaurate (DBTL)).

The above list is given only to illustrate some examples of the most common minor ingredients used in 10 rubber mixtures, particularly in rubber mixtures for tyres, and shall not be intended as limitative of the scope of the present invention.

According to a preferred aspect, in the process of the present invention a first extruder and a second 15 extruder are provided, wherein by means of said first extruder an intermediate rubber mixture devoid of temperature sensitive minor ingredients is produced, and by means of said second extruder a complete rubber mixture including said temperature sensitive minor ingredients is 20 produced.

According to a preferred aspect, the thermoplastic binding agent has a melting temperature (T<sub>m</sub>) not lower than 40°C, preferably from 50°C to 120°C. The melting temperature may be determined according to known 25 techniques, e.g. by Differential Scanning Calorimetry (DSC).

More preferably, the thermoplastic binding agent comprises a polymer selected from:

(i) ethylene homopolymers or copolymers of ethylene 30 with at least one aliphatic or aromatic alpha-olefin, and optionally with at least one polyene;

(ii) copolymers of ethylene with at least one ethylenically unsaturated ester;

(iii) polymers obtained by methatesis reaction of at 35 least one cycloalkene;  
or mixtures thereof.

With reference to the polymer (i), with alpha-olefin

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is generally meant an olefin of formula  $\text{CH}_2=\text{CH}-\text{R}$ , where R is:

an alkyl group, linear or branched, having from 1 to 12 carbon atoms; or

5 an aryl group having from 6 to 14 carbon atoms.

Preferably, the aliphatic alpha-olefin is selected from: propylene, 1-butene, isobutene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-dodecene, or mixtures thereof. Preferably, the aromatic alpha-olefin is selected

10 from styrene, alpha-methyl-styrene, or mixtures thereof.

Preferably, the polyene optionally present as comonomer of the polymer (i) is a conjugated or non-conjugated diene, triene or tetraene, having generally from 4 to 20 carbon atoms. The polyene is preferably selected from: 1,3-butadiene, 1,4-hexadiene, 1,6-octadiene, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, vinylnorbornene, or mixtures thereof.

The polymer (i) generally has the following monomer composition: 50%-100% by mole, preferably 60%-97% by mole, of ethylene; 0%-50% by mole, preferably 3%-40% by mole, of an aliphatic or aromatic alpha-olefin; 0%-5% by mole, preferably 0%-2% by mole, of a polyene.

According to a preferred embodiment, the polymer (i) is a copolymer of ethylene with at least one aliphatic or aromatic alpha-olefin, and optionally with at least one polyene, having a molecular weight distribution index (MWD) lower than 5, preferably from 1.5 to 3.5. It may be obtained by copolymerization of ethylene with an aliphatic or aromatic alpha-olefin, and optionally a polyene, in the presence of a single-site catalyst, for instance a metallocene catalyst or a Constrained Geometry Catalyst.

Suitable metallocene catalysts are, for instance, coordination complexes of a transition metal, usually of Group IV, particularly titanium, zirconium or hafnium, with two cyclopentadienyl ligands, optionally substituted, used in combination with a co-catalyst, for instance an

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alumoxane, preferably a methylalumoxane, or a boron compound. See, e.g., *Adv. Organomet. Chem.*, Vol. 18, pag. 99, (1980); *Adv. Organomet. Chem.*, Vol. 32, pag. 325, (1991); *J.M.S. - Rev. Macromol. Chem. Phys.*, Vol. C34(3), pag. 439, (1994); *J. Organometallic Chemistry*, Vol. 479, pagg. 1-29, (1994); *Angew. Chem. Int.*, Ed. Engl., Vol. 34, pag. 1143, (1995); *Prog. Polym. Sci.*, Vol. 20, pag. 459 (1995); *Adv. Polym. Sci.*, Vol. 127, pag. 144, (1997); US Patent No. 5,229,478, or patent applications WO 93/19107, EP-35,342, EP-129,368, EP-277,003, EP-277,004, EP-632,065; *Macromol. Rapid. Commun.*, Vol. 17, pagg. 745-748, (1996); *Makromol. Chem.*, Vol. 191, pag. 2378-2396, (1990).

Suitable Constrained Geometry Catalyst are, for instance, coordination complexes of a metal, usually of Groups 3-10 or of Lanthanide series, with only one cyclopentadienyl ligand, optionally substituted, used in combination with a co-catalyst, for instance an alumoxane, preferably a methylalumoxane, or a boron compound (see, e.g., *Organometallics*, Vol. 16, pag. 3649, (1997); *J. Am. Chem. Soc.*, Vol. 118, pag. 13021, (1996); *J. Am. Chem. Soc.*, Vol. 118, pag. 12451, (1996); *J. Organometallic Chemistry*, Vol. 482, pag. 169, (1994); *J. Am. Chem. Soc.*, Vol. 116, pag. 4623, (1994); *Organometallics*, Vol. 9, pag. 867, (1990); US Patents No. 5,096,867 and No. 5,414,040, or patent applications WO 92/00333, WO 97/15583, WO 01/12708, EP-416,815, EP-418,044, EP-420,436, EP-514,828; *Macromol. Chem. Phys.*, Vol. 197, pag. 1071-1083, (1996); *Macromolecules*, Vol. 32, pag. 7587-7593; patent applications WO 01/112078, EP-514,828, EP-416,815.

The above ethylene copolymers have preferably the following properties:

- density of from 0.86 g/cm<sup>3</sup> to 0.93 g/cm<sup>3</sup>;
- Mooney viscosity ML (1+4) at 125°C, measured according to ASTM Standard D1646-00, generally not lower than 5, preferably from 8 to 40;
- Melt Flow Index (MFI), measured according to ASTM Standard D1238-00, of from 0.1 g/10' to 35 g/10',

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preferably from 1 g/10' to 20 g/10';

- melting temperature ( $T_m$ ) of from 50°C to 120°C, preferably from 55°C to 110°C;

- melting enthalpy ( $\Delta H_m$ ) of from 30 J/g to 150 J/g,

5 preferably from 34 J/g to 130 J/g.

Examples of preferred ethylene copolymers as defined above are commercial products Engage® by DuPont-Dow Elastomers and Exact® by Exxon Chemical.

With reference to the polymer (ii), it is preferably 10 a copolymer of ethylene with at least one ethylenically unsaturated ester selected from: alkyl acrylates, alkyl methacrylates and vinyl carboxylates, wherein the alkyl group, linear or branched, may have from 1 to 8, preferably from 1 to 4, carbon atoms, while the 15 carboxylate group, linear or branched, may have from 2 to 8, preferably, from 2 to 5, carbon atoms. The ethylenically unsaturated ester is present in the polymer (ii) generally in an amount of from 5% to 50% by weight, preferably from 15% to 40% by weight. Examples of 20 acrylates or methacrylates are: ethyl acrylate, methyl acrylate, methyl methacrylate, t-butyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate. Examples of vinyl carboxylates are: vinyl acetate, vinyl propionate, vinyl butanoate. Preferably, the polymer (ii) 25 is selected from: ethylene/vinylacetate copolymer (EVA), ethylene/ethylacrylate copolymer (EEA); ethylene/butylacrylate copolymer (EBA).

With reference to the polymer (iii), it may be obtained according to known techniques, by methatetis 30 reaction, in solution, of a cycloalkene such as, for instance, cyclopentene, cyclooctene, cyclododecene. Further details on the preparation of such polymers are described, e.g., by Scott, Calderon, Ofstead, Judy and Ward in *Rubber Chem. and Tech.*, 44 (1971), and in US 35 Patents No. 3,816,358 and No. 4,153,772.

Preferably, the polymer (iii) has the following properties:

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- percentage of double bonds in trans configuration, determined by infrared (IR) spectroscopy, of at least 60% by mole, preferably from 75% to 95% by mole;
- Mooney viscosity ML (1+4) at 125°C, measured according 5 to ASTM Standard D1646-00, of from 2 to 20, preferably from 5 to 15;
- melting temperature (T<sub>m</sub>), measured by DSC, of from 25°C to 80°C, preferably from 40°C to 60°C;
- glass transition temperature (T<sub>g</sub>), measured according to 10 DIN Standard 53445, of from -90°C to -50°C, preferably from -80°C to -60°C.

As polymer (iii) polyoctenamer is particularly preferred, e.g. one of those commercially available under the trademark Vestenamer® by Degussa-Hüls.

15 The thermoplastic binding agent according to the present invention may be used in admixture with at least one elastomeric polymer, having a glass transition temperature (T<sub>g</sub>) lower than 20°C, preferably from 0°C to -90°C. The addition of at least one elastomeric polymer may 20 improve resistance of the subdivided product to mechanical stresses, particularly to impacts. The amount of the elastomeric polymer may be generally of from 0 to 40% by weight, preferably from 10% to 20% by weight, with respect to the weight of the minor ingredient present in the 25 subdivided product.

The elastomeric polymer may be generally selected from: diene elastomeric polymers and mono-olefin elastomeric polymers.

30 Diene elastomeric polymers are generally of natural origin, or may be obtained by polymerization, in solution or in emulsion, of at least one conjugated diolefin, optionally with at least one monovinylarene in an amount not exceeding 50% by weight. Examples of diene elastomeric polymers are: cis-1,4-polyisoprene (either natural or 35 synthetic, preferably natural rubber), 3,4-polyisoprene, polychloroprene, isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, 1,3-butadiene/styrene

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copolymers, isoprene/styrene copolymers, isoprene/1,3-butadiene/styrene terpolymers; or mixtures thereof.

As to mono-olefin elastomeric polymers, they may be selected from: copolymers of ethylene with at least one 5 alpha-olefin having from 3 to 12 carbon atoms, and optionally with a diene having from 4 to 12 carbon atoms; polyisobutene; copolymers of isobutene with at least one diene. Particularly preferred are: ethylene/propylene copolymers (EPR); ethylene/propylene/diene terpolymers 10 (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers; or mixtures thereof.

To improve mechanical resistance of the subdivided product, at least one reinforcing filler may also be added to the thermoplastic binding agent, such as: carbon black, 15 silica, alumina, aluminosilicates, calcium carbonate, kaolin, titanium dioxide, or mixtures thereof. The amount of the reinforcing filler may be generally of from 0 to 60% by weight, preferably from 5% to 40% by weight, with respect to the weight of the minor ingredient present in 20 the subdivided product.

To improve dispersion of the minor ingredient into the thermoplastic binding agent, at least one plasticizing agent may be further added to the subdivided product. The plasticizing agent may be selected for instance from: 25 mineral oils, such as paraffinic oils, naphtenic oils, aromatic oils; vegetable oils; or mixtures thereof. The amount of the plasticizing agent may be generally of from 0 to 40% by weight, preferably from 5% to 10% by weight, with respect to the weight of the minor ingredient present 30 in the subdivided product.

The present invention is now further illustrated with reference to the attached figures wherein:

Figure 1a is a schematic diagram of the first part of a continuous production plant of rubber mixtures according 35 to the present invention, wherein the intermediate rubber mixture is produced;

Figure 1b is a schematic diagram of the second part

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of a continuous production plant of rubber mixtures according to the present invention, wherein the final curable rubber mixture is produced starting from the intermediate rubber mixture.

5 With reference to Figure 1a, the first part of the production plant, where the intermediate rubber mixture is produced, includes a rubber grinder (1) where the rubber base materials, which are usually provided by manufacturers in bales, are comminuted in irregular 10 particles (crumbs) of small size (about 3-50 mm as average dimensions), e.g. by means of blades. The rubber crumbs are then supplemented with an antisticking agent (e.g. chalk, silica, or other powders) and then introduced into rubber storage drums (2), where the rubber particles are 15 continuously or stepwise slowly rotated to prevent re-agglomeration. To obtain a continuous feeding of the rubber crumbs to the plant, usually at least two drums are used, which are alternately filled and discharged. The rubber crumbs are then conveyed, e.g. by means of a 20 conveyor belt, to a loss-in-weight gravimetric feeder (3), for metering the rubber materials and feed them to the main feed hopper (4) of the first extruder (5).

Using the same hopper (4) and/or through an additional feed hopper (6), reinforcing fillers are 25 introduced into the first extruder (5). The use of an additional feed hopper (6) (as represented in Figure 1a) allows to add the total amount of reinforcing fillers in portions at different points of the extruder (5), so as to improve dispersion of the fillers in the rubber base. In 30 the embodiment represented in Figure 1a, different types of carbon black may be conveyed from storage bins (7) to corresponding gravimetric feeders (8a, 8b), while different types of silica may be conveyed from other storage bins (9) to corresponding gravimetric feeders 35 (10a, 10b). The extruder (5) may be also provided with an additional gravimetric feeder (11) to feed, from a corresponding storage bin (12), those rubbers which are

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available in the form of powder. Gravimetrically controlled feeding pumps (13) are also provided to introduce into the extruder (5) plasticizing oils and possibly other liquid ingredients, such as silica coupling 5 agents (e.g. silanes) and adhesion promoters (e.g. cobalt salts).

At least one of the feed hoppers (4, 6) of the extruder (5) is provided with gravimetric feeders (14) to meter and feed subdivided products (e.g. granules) 10 containing the minor ingredients, according to the present invention. The granules are conveyed to the gravimetric feeders (14) from storage bins (15) by means of pneumatic conveying lines (16).

According to a preferred embodiment, each type of 15 granular product containing a specific minor ingredient (or a predetermined mixture of different minor ingredients) is individually conveyed, metered and fed by means of a dedicated pneumatic conveying line (16) and a dedicated gravimetric feeder (14). In that way, irregular 20 feeding and inaccurate metering deriving from different densities of the granules are prevented, since granules of the same density are fed to the extruder (5). Alternatively, to reduce metering errors due to a scarce filling of the gravimetric feeders (14), different 25 granular products may be metered and fed by means of the same gravimetric feeder (14).

The minor ingredients to be fed to the first extruder (5) are generally those ingredients which are not temperature sensitive, and therefore cannot degrade and/or 30 cause scorching. Moreover, it is to be avoided to feed to the first extruder (5) those minor ingredients which can interfere with reactions which may occur during the first mixing stage. For instance, in the case of silica filled rubber mixtures, zinc derivatives (e.g. ZnO) and amine 35 compounds are added only during the second mixing step, since they can interfere with the silanization reaction between the coupling agent and silica. Generally, in the

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first extruder (5) all the minor ingredients are fed except: crosslinking agents, crosslinking accelerators, crosslinking retardants, and crosslinking activators.

The intermediate rubber mixture is discharged from 5 the first extruder (5) through a die (17). Preferably, before leaving the first extruder, the intermediate rubber mixture is filtered to eliminate possible aggregates, metal particles or other impurities. To that purpose, a filtering body (18) (e.g. a screen filter) is placed 10 before the die (17). To impart to the extruded material a pressure sufficient to pass the filtering body (18), a gear pump (19) is preferably placed upstream of the filtering body (18).

Referring now to Figure 1b, the intermediate rubber 15 mixture discharged from the first extruder (5) is then conveyed to the second extruder (20), where the rubber mixture is completed with the temperature sensitive ingredients. The passage of the rubber mixture from the first to the second extruder may be performed according to 20 any known method, and should be used to cool down the intermediate mixture to avoid rubber scorching during the second mixing step. For instance, the passage from the first to the second extruder may be obtained by a "loose" connection, for instance by festoons of the intermediate 25 rubber mixture extruded in the form of a continuous strip or sheet. Preferably, the intermediate rubber mixture is granulated, e.g. by passing it through a perforated die plate equipped with blades (not represented in the figures).

30 The intermediate rubber mixture is conveyed, e.g. by means of a conveyor belt, to a loss-in-weight gravimetric feeder (21) for metering and feeding to the second extruder (20) through a feed hopper (22). Through the same feed hopper (21) (or preferably through an additional feed 35 hopper - not represented in Figure 1b), the minor ingredients necessary to complete the rubber mixture are fed to the extruder (20). According to the present

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invention, said minor ingredients are used in the form of subdivided products (e.g. granules). The granules are conveyed from storage bins (23) to gravimetric feeders (24) by means of pneumatic conveying lines (25).  
5 Analogously to the first phase of the production process, preferably each type of granular product containing a specific minor ingredient (or a predetermined mixture of different minor ingredients) is individually conveyed, metered and fed by means of a dedicated pneumatic  
10 conveying line (25) and a dedicated gravimetric feeder (24). Alternatively, different granular products may be metered and fed by means of the same gravimetric feeder (24). As represented in Figure 1b, after metering, different granular products may be fed to additional  
15 hoppers (26) which convey the granular products to the extruder hopper (22).

The minor ingredients to be fed to the second extruder (20) in the form of subdivided products are generally those ingredients, necessary to complete the  
20 rubber mixture, which are temperature sensitive, such as crosslinking agents, crosslinking accelerators and retardants, activating agents.

The second extruder (20) may be also provided with gravimetrically controlled feeding pumps (27) to introduce  
25 into the extruder (20) additional plasticizing oils or other liquid ingredients, such as liquid resins (e.g. phenolic resins) and anti-reversion agents (e.g. silanes).

The final rubber mixture is discharged from the second extruder (20) through a die (28). Analogously to  
30 the first production phase, the final rubber mixture may be optionally filtered to eliminate possible aggregates, metal particles or other impurities. Therefore, a filtering body (29) (e.g. a screen filter) and a gear pump (30) may be placed before the die (28). During this  
35 optional filtering phase of the completed rubber mixture, particular care should be taken to avoid temperature raising which could cause scorching of the rubber.

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The pneumatic conveying lines (16, 25) are connected to a pneumatic conveying system (not represented in the figures) which may be implemented according to techniques well known in the art. In general terms, a pneumatic conveying system is able to transport a subdivided product through a pipeline using the motive force of air (or any other gas) under a positive or negative pressure.

A pneumatic conveying system suitable for the present invention may operate in "dilute phase" or in "dense phase", namely with a low filling factor or with a high filling factor of the pneumatic line. In the case of a dilute phase conveying system, the product to be transported is suspended in the air stream and the conveying velocity is high (usually from 15 to 40 m/sec), while in a dense phase system the product slides through the pipeline rather than particles being fully suspended in the air stream, and the conveying velocity is low (usually not higher than 5-10 m/sec).

The pneumatic conveying system usually comprises a blower or a fan to deliver air into the pipeline (in the case of a positive pressure) or to suck air from the pipeline (in the case of a negative pressure), a feed device to entrain the product into the conveying air (e.g. a rotary valve) and a filter or air separator to remove the product from the air at the receiving device (e.g. a feed hopper). For a survey on pneumatic conveying systems, see for instance the paper "Recent Developments In Pneumatic Conveying" by R. L. Serpan, presented at the PCA/MTC Technical Session (Sept. 22, 1998, Banff, Alberta 30 Canada).

The process according to the present invention may be employed to produce rubber mixture of any kind of elastomers, particularly of elastomers used in the tyre industry. Generally, the elastomeric base may be selected from: diene elastomeric polymers and mono-olefin elastomeric polymers, or mixtures thereof.

Diene elastomeric polymers are generally of natural

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origin, or may be obtained by polymerization, in solution or in emulsion, of at least one conjugated diolefin, optionally with at least one monovinylarene in an amount not exceeding 50% by weight. Examples of diene elastomeric polymers are: cis-1,4-polyisoprene (either natural or synthetic, preferably natural rubber), 3,4-polyisoprene, poly-1,3-butadiene (in particular, high vinyl poly-1,3-butadiene having a content of 1,2-polymerized units of from 15% to 85% by weight), polychloroprene, optionally halogenated isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, 1,3-butadiene/styrene copolymers, 1,3-butadiene/isoprene copolymers, isoprene/styrene copolymers, isoprene/1,3-butadiene/styrene terpolymers; or mixtures thereof.

As to mono-olefin elastomeric polymers, they may be selected from: copolymers of ethylene with at least one alpha-olefin having from 3 to 12 carbon atoms, and optionally with a diene having from 4 to 12 carbon atoms; polyisobutene; copolymers of isobutene with at least one diene. Particularly preferred are: ethylene/propylene copolymers (EPR); ethylene/propylene/diene terpolymers (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers; or mixtures thereof.

The rubber mixture further comprises at least one reinforcing filler, such as: carbon black, silica, alumina, aluminosilicates, calcium carbonate, kaolin, titanium dioxide, or mixtures thereof. Particularly preferred are carbon black and silica, or mixtures thereof. The amount of the reinforcing filler may be generally of from 0.1 to 120 phr, preferably from 20 to 90 phr (phr = parts by weight per 100 parts by weight of elastomeric base).

To improve processability, at least one plasticizing agent is preferably added to the rubber mixtures. It is generally selected from mineral oils, vegetable oils, synthetic oils and the like, or mixtures thereof, for instance: aromatic oil, naphthene oil, phthalates, soybean

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oil, or mixtures thereof. The amount of the plasticizing agent may generally range from 2 to 100 phr, preferably from 5 to 50 phr.

5 The present invention is now further illustrated by the following working examples.

Preparation of minor ingredients in the granular form.

Some minor ingredients were produced in the granular form, by mixing each minor ingredient with the binding agent in a co-rotating twin-screw extruder. The extruded 10 material, in the form of "spaghetti", was cooled in a water bath, dried with an air flow and chopped, so as to obtain granules having the following dimensions: about 2 mm diameter, about 3 mm length.

15 The compositions of the different granules are reported in Table 1 (the percentages are expressed by weight with respect to the total weight of the granules).

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Table 1

| Ingredient   | Binding agent                                  |
|--|--|
| Stearic Acid (70%)   | Engage® 8200 (20%)<br>Carbon black N660 (10%)  |
| ZnO (85%)  | Engage® 8150 (7.5%)<br>Vestenamer® 8012 (7.5%) |
| Wax (50%)  | Engage® 8200 (30%)<br>Carbon black N660 (20%)  |
| N-cycloexylmercaptobenzo-thiazylsulphenamide (CBS) (70%)                               | Engage® 8150 (30%)                             |
| N-tertbutyl-mercaptobenzothiazyl sulphenamide (TBBS) (70%)                             | Engage® 8150 (30%)                             |
| N,N-dicycloexylmercaptobenzo-thiazyl sulphenamide (DCBS) (70%)                         | Engage® 8150 (30%)                             |
| Insoluble sulfur (S <sub>n</sub> ) (76.5%)   | Engage® 8150 (15%)<br>Paraffin Oil (8.5%)      |
| Insoluble sulfur (S <sub>n</sub> ) + N-cyclohexyl thiophtaloimide (PVI) (6:1 wt) (79%) | Engage® 8150 (15%)<br>Paraffin Oil (6%)        |
| Diphenyl guanidine (DPG) (70%)   | Engage® 8150 (30%)                             |

5       Engage® 8200 (by Du Pont-Dow Elastomers): ethylene/1-octene copolymer obtained by metallocene catalysis having the following characteristics:

ethylene/1-octene weight ratio = 76/24; density = 0.870 g/cm<sup>3</sup>; MFI = 0.5 g/10',  $\Delta H_m$  = 24 J/g;  $T_m$  = 60°C.

10      Engage® 8150 (by Du Pont-Dow Elastomers): ethylene/1-octene copolymer obtained by metallocene catalysis having the following characteristics:

ethylene/1-octene weight ratio = 75/25; density = 0.868 g/cm<sup>3</sup>; MFI = 0.5 g/10',  $\Delta H_m$  = 34.8 J/g;  $T_m$  = 59.2°C.

EXAMPLE 1.

A rubber mixture was prepared by means of an apparatus with a configuration as illustrated in Figures 5 1a and 1b, using natural rubber (NR) as elastomeric base and carbon black as reinforcing filler. The composition of the rubber mixture is reported in Table 2 (the values reported in the table refer to the amount of active ingredient, without taking into account the binding 10 agent).

To prepare the intermediate rubber mixture, a co-rotating intermeshing twin screw extruder was employed, having a cylinder diameter of 58 mm and a L/D ratio of 48. The NR was first granulated using a rotating blades mill, 15 to an average particle size about 1 cm, and dusted with silica in order to prevent reagglomeration. The granulated NR was fed through the main hopper of the extruder, together with carbon black. Through the same hopper, ZnO and stearic acid were fed in the form of granules, whose 20 compositions are reported in Table 1. Each granular ingredient was fed using a dedicated gravimetric feeder; the reservoir refill of the feeders was carried out by means of the pneumatic conveying lines, as represented in Figure 1a. Aromatic oil was injected into the extruder 25 through the second hopper. The temperature of the extruded material was 167°C.

The intermediate rubber mixture extruded in the first stage was granulated and dusted with silica, then fed through the main hopper of a second 58 mm extruder 30 (L/D=48). The curatives (insoluble sulfur and N,N-dicyclohexyl mercapto-benzothiazyl sulphenamide (DCBS)), were fed through the main hopper of the second extruder in the form of granules, whose composition is reported in Table 1. Each granular ingredient was fed using a 35 dedicated gravimetric feeder; the reservoir refill of the feeders was carried out by means of the pneumatic conveying lines, as represented in Figure 1b. The

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protective agent (N-(1,3-dimethyl)butyl-N'-phenyl-p-phenylenediamine) was injected into the second extruder in the molten state by means of a feeding pump. The temperature of the extruded material was 117°C.

5 The Mooney viscosity ML(1+4) at 100°C of the so obtained rubber mixture was measured according to Standard ISO 289/1. The mechanical properties (according to ISO standard 37) and the hardness in IRHD degrees at 23°C and 100°C (according to ISO standard 48) were measured on 10 samples of the composition cross-linked at 170°C for 10 minutes. The results are shown in Table 3.

Table 3 also shows the dynamic elastic properties, measured with a dynamic Instron device in the traction-compression mode according to the following method. A test 15 piece of the cross-linked material having a cylindrical form (length = 25 mm; diameter = 14 mm), compression-preloaded up to a 10% longitudinal deformation with respect to the initial length, and kept at the prefixed temperature (70°C or 23°C) for the whole duration of the 20 test, was submitted to a dynamic sinusoidal strain having an amplitude of  $\pm 3.33\%$  with respect to the length under pre-load, with a 100 Hz frequency. The dynamic elastic properties are expressed in terms of dynamic elastic modulus -(E') and tandelta (loss factor) values. As is 25 known, the tandelta value is calculated as a ratio between the viscous modulus (E'') and the elastic modulus (E'), both of them being determined with the above dynamic measurements.

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Table 2

| Ingredients             | phr   |
|-------------------------|-------|
| First stage             |       |
| Natural Rubber (STR 20) | 100   |
| Carbon Black N375       | 60    |
| Aromatic Oil            | 7     |
| Zinc Oxide *            | 3.5   |
| Stearic Acid *          | 2     |
| Second stage            |       |
| DCBS *                  | 1.3   |
| Sulfur *                | 2     |
| 6PPD                    | 2     |
| Total parts             | 177.8 |

\* fed in the granular form

5

Table 3

| Test                     | Value |
|--------------------------|-------|
| Viscosity ML(1+4) @100°C | 71.3  |
| 100% Modulus (MPa)       | 1.54  |
| 300% Modulus (MPa)       | 8.33  |
| Stress at break (MPa)    | 18.15 |
| Elongation at break (%)  | 517.5 |
| E' @23°C (MPa)           | 3.91  |
| E' @70°C (MPa)           | 3.13  |
| Tandelta @23°C           | 0.174 |
| Tandelta @70°C           | 0.135 |
| IRHD Hardness @23°C      | 56    |
| IRHD Hardness @100°C     | 49    |

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EXAMPLE 2.

A rubber mixture was prepared by means of an apparatus with a configuration as illustrated in Figures 1a and 1b, using a mixture of styrene/butadiene copolymer (SBR) and polybutadiene (BR) as elastomeric base and silica as reinforcing filler. The composition of the rubber mixture is reported in Table 4 (the values reported in the table refer to the amount of active ingredient, without taking into account the binding agent).

To prepare the intermediate rubber mixture, a co-rotating intermeshing twin screw extruder was employed, having a cylinder diameter of 58 mm and a L/D ratio of 48. The SBR and BR were first granulated using a rotating blades mill, to an average particle size about 1 cm, and dusted with silica in order to prevent reagglomeration, then a physical blend of the so obtained crumbs was made. The blend of the granulated rubbers was fed through the main hopper of the extruder, together with silica. Through the same hopper, wax and stearic acid were fed in the form of granules, whose compositions are reported in Table 1. Each granular ingredient was fed using a dedicated gravimetric feeder; the reservoir refill of the feeders was carried out by means of the pneumatic conveying lines, as represented in Figure 1a. As coupling agent for silica, the commercial product X50S by Degussa was used (consisting of 50% by weight of bis(3-triethoxysilylpropyl)tetrasulfide and 50% by weight of carbon black).

Aromatic oil was injected into the extruder through the second hopper. The temperature of the extruded material was 150°C.

The intermediate rubber mixture extruded in the first stage was granulated and dusted with silica, then fed through the main hopper of a second 58 mm extruder (L/D=48). The curatives (insoluble sulfur, N-cycloexyl mercapto-benzothiazyl sulphenamide (CBS) and diphenyl guanidine (DPG)), were fed through the main hopper of the

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second extruder in the form of granules, whose composition is reported in Table 1. Each granular ingredient was fed using a dedicated gravimetric feeder; the reservoir refill of the feeders was carried out by means of the pneumatic 5 conveying lines, as represented in Figure 2. The protective agent (N-(1,3-dimethyl)butyl-N'-phenyl-p-phenylenediamine) was injected into the second extruder in the molten state by means of a feeding pump. The temperature of the extruded material was 128°C.

10 The so obtained rubber mixture was characterized as reported in Example 1. The results are shown in Table 5.

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Table 4

| Ingredients           | phr   |
|-----------------------|-------|
| First stage           |       |
| s-SBR (JSR HP-752)    | 70    |
| BR (Buna® Cis-132)    | 30    |
| Silica (Zeosil® 1165) | 65    |
| Aromatic Oil          | 7     |
| Coupling agent        | 10    |
| Wax *                 | 1.5   |
| Stearic Acid *        | 2     |
| Second stage          |       |
| Zinc Oxide *          | 2.5   |
| DPG *                 | 1     |
| CBS *                 | 2     |
| Sulfur *              | 1.2   |
| 6PPD                  | 2     |
| Total parts           | 194.2 |

\* fed in the granular form

Table 5

| Test                     | Value |
|--------------------------|-------|
| Viscosity ML(1+4) @100°C | 80.1  |
| 100% Modulus (MPa)       | 2.90  |
| 300% Modulus (MPa)       | 12.88 |
| Stress at break (MPa)    | 18.26 |
| Elongation at break (%)  | 439.1 |
| E' @23°C (MPa)           | 10.78 |
| E' @70°C (MPa)           | 7.15  |
| Tandelta @23°C           | 0.299 |
| Tandelta @70°C           | 0.137 |
| IRHD Hardness @23°C      | 76    |
| IRHD Hardness @100°C     | 69    |

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EXAMPLE 3.

A rubber mixture was prepared by means of an apparatus with a configuration as illustrated in Figures 1a and 1b, using a mixture of natural rubber (NR) and 5 polybutadiene (BR) as elastomeric base and carbon black as reinforcing filler. The composition of the rubber mixture is reported in Table 6 (the values reported in the table refer to the amount of active ingredient, without taking into account the binding agent).

10 To prepare the intermediate rubber mixture, a co-rotating intermeshing twin screw extruder was employed, having a cylinder diameter of 58 mm and a L/D ratio of 48. The NR and BR were first granulated using a rotating blades mill, to an average particle size about 1 cm, and 15 dusted with silica in order to prevent reagglomeration, than a physical blend of the so obtained crumbs was made. The blend of the granulated rubbers was fed through the main hopper of the extruder, together with carbon black. Through the same hopper, zinc oxide, wax and stearic acid 20 were fed in the form of granules, whose compositions are reported in Table 1. Each granular ingredient was fed using a dedicated gravimetric feeder; the reservoir refill of the feeders was carried out by means of the pneumatic conveying lines, as represented in Figure 1a. The 25 temperature of the extruded material was 146°C.

The intermediate rubber mixture extruded in the first stage was granulated and dusted with silica, then fed through the main hopper of a second 58 mm extruder (L/D=48). The curatives (insoluble sulfur + N-cyclohexyl 30 thiophtalimide (PVI) and N-tertbutyl-mercaptobenzothiazyl sulphenamide (TBBS)), were fed through the main hopper of the second extruder in the form of granules, whose composition is reported in Table 1. Each granular ingredient was fed using a dedicated gravimetric feeder; 35 the reservoir refill of the feeders was carried out by means of the pneumatic conveying lines, as represented in Figure 1b. The protective agent (N-(1,3-dimethyl)butyl-N'-

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phenyl-p-phenylenediamine) was injected into the second extruder in the molten state by means of a feeding pump. The temperature of the extruded material was 128°C.

5 The so obtained rubber mixture was characterized as reported in Example 1. The results are shown in Table 7.

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Table 6

| Ingredients             | phr   |
|-------------------------|-------|
| First stage             |       |
| Natural Rubber (STR 20) | 50    |
| BR (Buna® Cis-132)      | 50    |
| Carbon Black N660       | 50    |
| Zinc Oxide *            | 3     |
| Wax *                   | 2     |
| Stearic Acid *          | .2    |
| Second stage            |       |
| TBBS *                  | 0.8   |
| Sulfur *                | 1.8   |
| PVI *                   | 0.3   |
| 6PPD                    | 2.5   |
| Total parts             | 162.4 |

\* fed in the granular form

Table 7

| Test                     | Value |
|--------------------------|-------|
| Viscosity ML(1+4) @100°C | 65.2  |
| 100% Modulus (MPa)       | 2.08  |
| 300% Modulus (MPa)       | 8.92  |
| Stress at break (MPa)    | 14.18 |
| Elongation at break (%)  | 459.0 |
| E' @23°C (MPa)           | 5.30  |
| E' @70°C (MPa)           | 4.28  |
| Tandelta @23°C           | 0.142 |
| Tandelta @70°C           | 0.111 |
| IRHD Hardness @23°C      | 61    |
| IRHD Hardness @100°C     | 58    |

## CLAIMS.

1. A process for continuously producing an elastomeric composition, comprising the steps of:
  - 5 - providing at least one extruder comprising a housing, at least one screw rotatably mounted in said housing, said housing including at least one feed opening and a discharge opening;
  - 10 - metering and feeding into said at least one extruder at least one elastomer and at least one filler;
  - metering and feeding into said at least one extruder minor ingredients different from elastomers and fillers;
  - mixing and dispersing said at least one filler and minor ingredients into said at least one elastomer by 15 means of said at least one extruder;
  - extruding the resulting elastomeric composition through said discharge opening;

wherein at least one of said minor ingredients is conveyed, before metering and feeding into the extruder, 20 by means of a pneumatic conveying line in the form of a subdivided product, said product including said at least one minor ingredient dispersed in at least one thermoplastic binding agent.
2. Process according to claim 1, wherein at least one 25 plasticizing agent is further metered and fed into the extruder.
3. Process according to claim 1 or 2, wherein the subdivided product is metered and fed by means of a gravimetric feeder.
- 30 4. Process according to anyone of the previous claims, wherein the subdivided product contains from 40% to 98% by weight of said at least one minor ingredient, with respect to the total weight of said product.
- 35 5. Process according to claim 4, wherein the subdivided product contains from 50% to 95% by weight of said at least one minor ingredient, with respect to the

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total weight of said product.

6. Process according to claim 5, wherein the subdivided product contains from 70% to 85% by weight of said at least one minor ingredient, with respect to the 5 total weight of said product.

7. Process according to anyone of the previous claims, wherein the subdivided product has a Shore A hardness not lower than 45 and a Shore D hardness not greater than 65.

10 8. Process according to claim 7, wherein the subdivided product has a Shore D hardness of from 20 to 60.

9. Process according to anyone of the previous claims, wherein said at least one minor ingredient which 15 is metered and fed in the form of a subdivided product is selected from: crosslinking agents, crosslinking accelerators, synthetic resins, crosslinking activators, crosslinking retardants, adhesion promoters, protective agents, coupling agents, condensation catalysts.

20 10. Process according to anyone of the previous claims, wherein a first extruder and a second extruder are provided, by means of said first extruder producing an intermediate rubber mixture devoid of temperature sensitive minor ingredients, and by means of said second 25 extruder producing a complete rubber mixture including said temperature sensitive minor ingredients.

11. Process according to claim 10, wherein said temperature sensitive minor ingredients are selected from: crosslinking agents, crosslinking accelerators, 30 crosslinking retardants, and crosslinking activators.

12. Process according to anyone of the previous claims, wherein the thermoplastic binding agent has a melting temperature (T<sub>m</sub>) not lower than 40°C.

13. Process according to claim 12, wherein the 35 thermoplastic binding agent has a melting temperature (T<sub>m</sub>) of from 50°C to 120°C.

14. Process according to anyone of the previous

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claims, wherein the thermoplastic binding agent comprises a polymer selected from:

- (i) ethylene homopolymers or copolymers of ethylene with at least one aliphatic or aromatic alpha-olefin, and 5 optionally with at least one polyene;
- (ii) copolymers of ethylene with at least one ethylenically unsaturated ester;
- (iii) polymers obtained by metathesis reaction of at least one cycloalkene;

10 or mixtures thereof.

15. Process according to claim 14, wherein the thermoplastic binding agent comprises a copolymer of ethylene with at least one aliphatic or aromatic alpha-olefin, and optionally with at least one polyene, having a 15 molecular weight distribution index (MWD) lower than 5.

16. Process according to claim 15, wherein the thermoplastic binding agent comprises a copolymer of ethylene with at least one aliphatic or aromatic alpha-olefin, and optionally with at least one polyene, having a 20 molecular weight distribution index (MWD) of from 1.5 to 3.5.

17. Process according to claim 15 or 16, wherein the copolymer is obtained by copolymerization of ethylene with an aliphatic or aromatic alpha-olefin, and optionally a 25 polyene, in the presence of a single-site catalyst.

18. Process according to anyone of the previous claims, wherein the thermoplastic binding agent is in admixture with at least one elastomeric polymer, having a glass transition temperature (Tg) lower than 20°C.

30 19. Process according to anyone of the previous claims, wherein the thermoplastic binding agent is in admixture with at least one reinforcing filler.

35 20. Process according to anyone of the previous claims, wherein the thermoplastic binding agent is in admixture with at least one plasticizing agent.

21. Apparatus for continuously producing an elastomeric composition, comprising:

- 37 -

- at least one extruder comprising a housing, at least one screw rotatably mounted in said housing, said housing including at least one feed opening and a discharge opening;
- 5 - at least one first metering device to meter and feed into said at least one extruder at least one elastomer and at least one filler through said at least one feed opening;
- at least one second metering device to meter and feed
- 10 into said at least one extruder minor ingredients different from elastomers and fillers, at least one of said minor ingredients being in the form of a subdivided product including said at least one minor ingredient dispersed in at least one thermoplastic binding agent;
- 15 - at least one pneumatic conveying line to convey said at least one minor ingredient in the form of a subdivided product from a storage bin to said at least one second metering device.

22. Apparatus according to claim 21, wherein a first

20 extruder and a second extruder are provided, by means of said first extruder producing an intermediate rubber mixture devoid of temperature sensitive minor ingredients, and by means of said second extruder producing a complete rubber mixture including said temperature sensitive minor

25 ingredients.

23. Apparatus according to claim 21 or 22, wherein at least one of said first and second metering devices is a gravimetric feeder.

24. Apparatus according to anyone of claims from 21

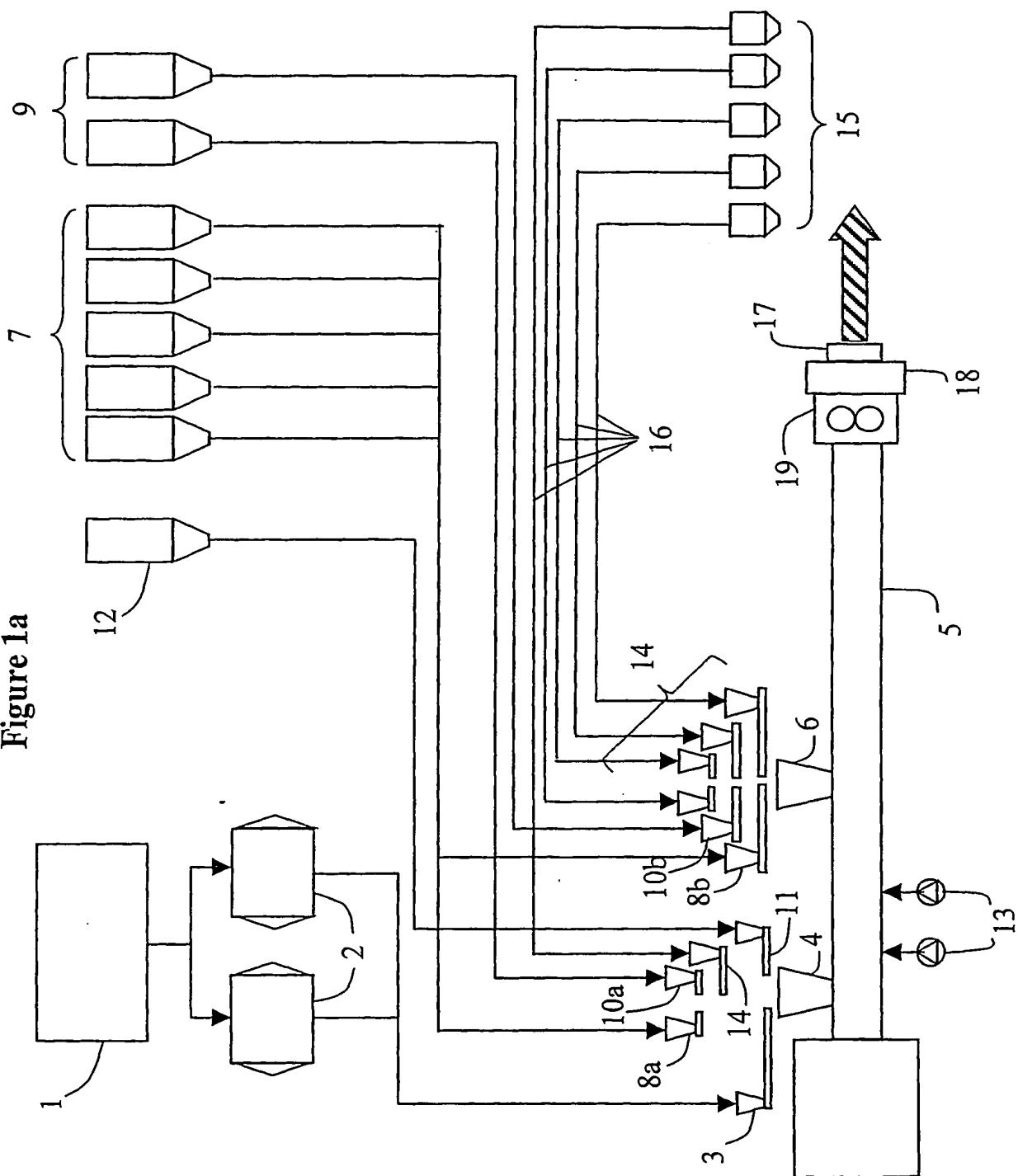
30 to 23, further comprising a rubber grinder to comminute said at least one elastomer before being metered and fed into said at least one extruder.

25. Apparatus according to anyone of claims from 21

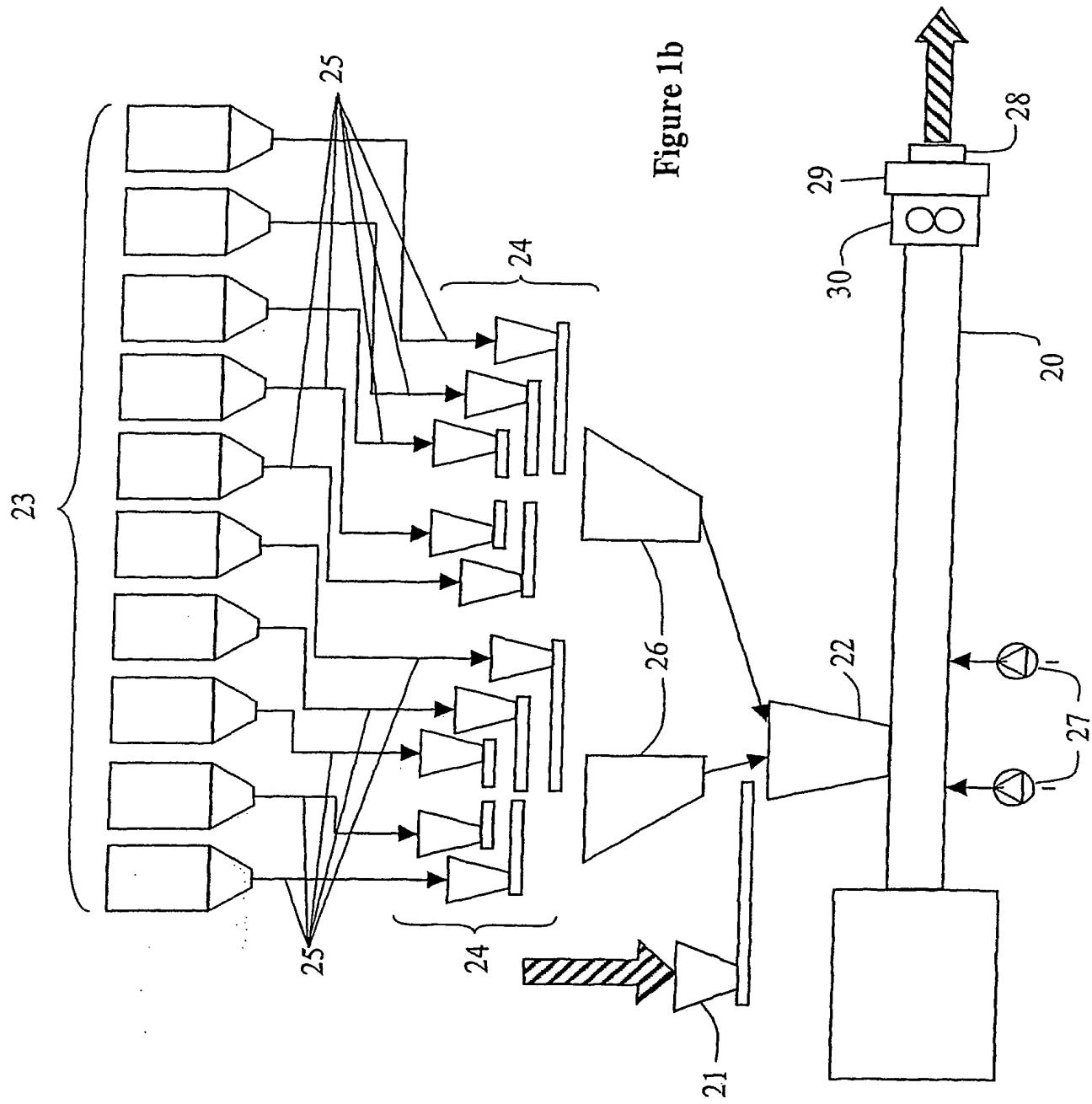
35 to 24, further comprising at least one filtering body to filter the elastomeric composition discharged from said at least one extruder.

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Figure 1a



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**INTERNATIONAL SEARCH REPORT**

International Application No  
PCT/EP 02/08145

|                                     |           |           |          |          |
|-------------------------------------|-----------|-----------|----------|----------|
| A. CLASSIFICATION OF SUBJECT MATTER |           |           |          |          |
| IPC 7                               | B29C47/10 | B29C31/02 | B29B7/88 | C08J3/22 |

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C B29B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages                                       | Relevant to claim No. |
|----------|--|-----------------------|
| X        | US 4 197 381 A (ALIA DOMINIC A)<br>8 April 1980 (1980-04-08)<br>column 8, line 50 -column 9, line 25;<br>figure 1<br>--- | 1-25                  |
| A        | US 5 711 904 A (HANDA PAWAN KUMAR ET AL)<br>27 January 1998 (1998-01-27)<br>figure 1<br>---                              | 1-25                  |
| A        | US 4 422 810 A (BORING DOUGLAS J)<br>27 December 1983 (1983-12-27)<br>column 1, line 1-19; claim 1<br>---                | 1                     |
| A        | US 3 352 952 A (MARR JOHN A)<br>14 November 1967 (1967-11-14)<br>figure 1<br>-----                                       | 1-25                  |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \*&\* document member of the same patent family

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|--|--|
| Date of the actual completion of the international search  | Date of mailing of the international search report |
| 12 September 2002  | 25/09/2002   |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br><br>Kofoed, J                |

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/08145

| Patent document cited in search report | Publication date | Patent family member(s) |               |               | Publication date                       |
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